IUPAC PERIODIC TABLE OF THE ISOTOPES- PRINCIPLES AND PRACTICAL APPLICATIONS

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OVERVIEW

The familiar Periodic Table of the Elements (PTE) found in most chemistry text books and on classroom walls illustrates important relations among the chemical elements. The design of the Periodic Table of the Elements highlights some of the systematic variations in electronic configurations and atomic weights of the different elements, and provides clues about their likely behavior in chemical reactions. In contrast, the IUPAC Periodic Table of the Isotopes has a different focus. Here we dig deeper into the subject of atomic weights and their variability. Whereas all atoms of an element have the same number of protons, atoms of a given element with different numbers of neutrons are called isotopes. For many elements that have more than one stable isotope, the atomic weights can be different depending on the material in which they occur; for example, carbon in plants typically has smaller atomic weight than carbon in the atmosphere. Such differences typically are small, but they can provide a wealth of information that is useful in science, industry, medicine, and many other fields. In addition, many isotopes are radioactive, and these forms present both hazards and benefits to mankind; for example, radioactivity can be used to generate power, diagnose disease, or determine the ages of archeological remains, but it can also cause cancer. In this report, we present background material related to the IUPAC Periodic Table of the Isotopes and discuss important features of the isotopes and how they are affecting our lives.

LEARNING OBJECTIVES

Having interacted with the range of materials associated with the IUPAC Periodic Table of the Isotopes, users should be able to:

Explain that elements are made up of different kinds of atoms called isotopes and that most elements have more than one stable isotope.

Calculate the atomic weight of an element from the abundances and atomic masses of the stable isotopes of that element.

Explain that the isotopic abundances of many elements are not constant and vary naturally, as well as by the influence of accidental and deliberate human activities.

Explain why the standard atomic weights of some elements are expressed as intervals.

Explain the causes of isotopic abundance variability.

Explain the difference between stable and radioactive isotopes, and how these properties are related to different practical applications.

Give examples of how isotopes are used in science, industry, and medicine.

TERMINOLOGY RELATED TO ISOTOPES AND ATOMIC WEIGHTS

[Quick summary of terminology used to describe atoms, isotopes, and atomic weights. Concepts and processes related to these terms are given in more detail in subsequent sections]

All **atoms** of a given chemical **element** have the same number of protons, which is equal to the **atomic number** and defines the chemical element. All atoms containing 6 protons are defined as atoms of carbon and designated $_6C$. But different atoms of the same element may have different numbers of neutrons. Atoms of an element with different numbers of neutrons are known as **isotopes** of the element, and are designated by the **isotope number**, which is the number of protons plus neutrons in the atom. For carbon in most substances on Earth, approximately 99 % of the atoms have 6 protons and 6 neutrons and are designated ^{12}C, whereas approximately 1 % of the atoms have 6 protons and 7 neutrons and are designated ^{13}C. Rarer carbon atoms have other numbers of neutrons. For a given element, different isotopes have different **atomic masses**, which depend on the number of protons and neutrons in the nucleus of the atom as well as how tightly the nucleus is bound, or how much energy is required to break the nucleus apart.

Depending on the nuclear configuration, or how the neutrons and protons interact in the nucleus of the atom, some isotopes are stable, whereas other isotopes are unstable and undergo **radioactive decay**. Although it is common practice to speak of radioactive elements, it is more correct to refer specifically to **radioactive isotopes**, as most elements have both stable and radioactive isotopes. Radioactive decay is a probabilistic process. We cannot say which atom in an assemblage of identical atoms will decay next, but we can predict that a certain portion of the atoms will likely decay over a certain period of time. The time it takes for one half of the total number of atoms of a radioactive isotope to decay is called the radioactive **half-life** of that isotope. Carbon atoms containing 8 neutrons, designated ^{14}C, are radioactive with half life of 5730 years. Naturally occurring ^{14}C is rare compared to the stable isotopes ^{12}C and ^{13}C; for example, leaves of modern plants typically have approximately one ^{14}C atom for every 10^{12} atoms of ^{12}C. Radioactive decay results in the generation of various products, some of which are **radiogenic isotopes** of the same or different elements (e.g., alpha particles, which are radiogenic ^4He atoms). Other decay products include gamma radiation, free neutrons, protons, electrons, and positrons.

The **atomic weight** (or relative atomic mass) of an element in a given sample is equal to the mean value of the atomic masses of all the individual stable atoms of that element in the sample. That is, the atomic weight depends on the atomic masses of the different isotopes and the relative numbers of the different isotopes in the sample. For example, if 99 % of the carbon atoms in a leaf were ^{12}C and 1 % of the atoms were ^{13}C, then the atomic weight of carbon in the leaf would be approximately 12.01, calculated from the relation (0.99 x 12) + (0.01 x 13.00335484) [Note: ^{12}C is unique in having an exact integer for its atomic mass, by convention]. Although all atoms of a given element have the same number of protons and can be expected to behave similarly during physical, chemical, and biologic processes, most such processes are also affected slightly by different atomic masses of an element, causing **isotope**

fractionation. Because of isotope fractionation, the relative abundances of ^{12}C and ^{13}C are not exactly the same in all materials on Earth, so the atomic weight of carbon is slightly different in different terrestrial samples. At present, the lowest and highest evaluated atomic weight values of carbon in different samples of normal terrestrial materials are 12.0096 and 12.0116, respectively. These values are presented as the carbon **atomic weight interval** in the IUPAC 2009 Table of Standard Atomic Weights {Wieser, 2011 #2848}. Atomic weight intervals for elements such as carbon are small enough to be ignored for some purposes; however, when the variations are measured precisely, they can provide a wealth of information about sources and processes affecting elements and compounds under natural and human influence, as described below.

The atomic weights are related to the definition of the **mole**, which is equal to the number of ^{12}C atoms in 12 grams of ^{12}C (defined by convention). This number, as determined recently from experimental measurements, is $6.02214078(18) \times 10^{23}$ ({Andreas, 2011 #2936}. For perspective on the huge number of particles this represents, imagine that one mole of ^{12}C atoms can be found in a small slice of a normal apple, whereas one mole of apples (8 cm in diameter) would fill all the oceans on Earth more than 150 times if packed tightly together. When speaking of isotopic abundances in this report, we refer to their **mole fractions** or **mole ratios** (or amount ratios); that is, the relative numbers of atoms with different atomic masses in a sample.

DESCRIPTION OF THE IUPAC PERIODIC TABLE OF THE ISOTOPES

[A brief description is given of the chart showing the IUPAC Periodic Table of the Isotopes (reproduced in Figure 1), based on the terminology summarized above. Causes and effects of variability in the isotopic compositions and atomic weights of the elements are given in more detail in subsequent sections]

The IUPAC Periodic Table of the Isotopes (IPTI) illustrates important features that are related to the abundances of the isotopes and corresponding variability of atomic weights of the elements. It is important to recognize that the atomic weights of many elements are not constants of nature. Also, it is important to realize that the abundances and properties of stable and radioactive isotopes are exploited pervasively in almost all branches of science, industry, and medicine, among other professions.

The IPTI indicates those elements that have no stable isotopes, only radioactive isotopes, for which no atomic weight is given (shown with white background). Other elements have one stable isotope and their atomic weights are invariant and are known with high precision (many significant digits), as indicated in the IPTI with light blue background color.

For elements with two or more stable isotopes, different samples could have different relative abundances of the stable isotopes and different atomic weights, as in the carbon example given above (this is true of all elements with yellow or pink background color). Although the atomic weight of such an element in a specific sample may be known precisely from measurement of isotope ratios in the sample, the atomic weights of the same element in different samples could have different values. Therefore, the atomic weights of samples that have not been analyzed

are not known precisely. This type of uncertainty is not the result of poor measurements, but rather the result of real variations among natural terrestrial samples of that element caused by various physical, chemical, and biological processes (see below). Some such elements exhibit atomic weight variations that exceed substantially the uncertainties of laboratory measurements. In some cases, these elements are presented with atomic-weight intervals and highlighted with pink background in the IPTI. Other elements with more than one stable isotope are indicated with yellow background and comprise two different groups: Some have known atomic-weight variations that exceed measurement uncertainties but have not yet been given atomic-weight intervals yet by IUPAC. Others have known or suspected atomic-weight variations but those variations are not significantly larger than the uncertainty of the best atomic weight measurements. In the latter case, the measured atomic weight of any single sample can serve as a proxy for the atomic weight of any other sample of normal terrestrial material. As evaluations proceed and measurement technology improves, some elements currently in the yellow categories are expected to be re-classified with intervals (as those in the pink category.

Isotopes provide an almost unlimited variety of useful tools for science, industry, medicine, and other activities. Useful radioactive isotopes include americium-241 (^{241}Am) in smoke detectors, technitium-99 (^{99}Tc) for imaging the internal organs of the human body for medical diagnosis, decay of uranium isotopes (^{235}U and ^{238}U) to lead isotopes (^{206}Pb and ^{207}Pb) for determining the ages of rocks and minerals. Applications of stable isotopes include boron-10 (^{10}B) used in boron neutron capture therapy for treating tumors of the brain, or measurements of stable isotope mole ratios such as carbon-13/carbon-12 (^{13}C/^{12}C) or oxygen-18/oxygen-16 (^{18}O/^{16}O) to detect "doping" in sports, authenticity of foods, effects of climate change, and origins of contaminants in the environment. It is important to note that differences in stable isotope amount ratios between two samples can be measured more precisely than the actual (absolute) isotope amount ratio of any sample can be measured. Therefore, many useful applications exist for differential isotope ratio measurements for some elements that do not have atomic-weight intervals in the IPTI. When measuring, describing, and applying stable isotopic variations, typically we refer to the isotope amount ratios (mole ratios) or the isotopic compositions of the elements, rather than the atomic weights.

In summary, the chemical elements consist of varying numbers of stable and/or radioactive isotopes, many of which have important applications to science and society. The atomic weights of many elements are not constant in nature, but vary because of different relative abundances of their stable isotopes in normal terrestrial materials.

The remainder of this document explains these concepts in more detail, with additional examples and figures. A companion document contains information about each of the elements, including the known isotopes and examples of their practical uses.

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ATOMIC WEIGHTS OF THE ELEMENTS- BEHIND THE SCENES

Introduction

A quick look at the IUPAC Periodic Table of the Isotopes will reveal that the atomic-weight values for some elements seem to be known precisely (single value with many significant digits), whereas others apparently are known with less precision (fewer significant digits). Closer inspection will reveal that some of the most common elements have the largest relative uncertainties in their atomic weights. In fact, many of them are expressed as intervals that cover a range of possibilities. Why is that? Shouldn't a common element like carbon have been measured more precisely than a relatively rare element like scandium?

Comparison of older and newer versions of the IUPAC Table of Standard Atomic Weights will reveal that the standard atomic weights of some elements have changed over the last few decades. In some cases, it's clear that new measurements have improved the accuracy and precision of the tabulated values, but in other cases, it seems the uncertainties actually have increased. Does that make sense? Shouldn't new measurements improve the uncertainties?

There are good answers to these questions, and the group responsible for sorting them out is the IUPAC Commission on Isotopic Abundances and Atomic Weights (CIAAW), which meets regularly to re-evaluate the Standard Atomic Weights of the elements.

What is the atomic weight of an element?

Each atom of each element has an "atomic mass" defined as 12 times the mass of the atom divided by the mass of a carbon-12 (12C) atom (for atoms at rest in nuclear and atomic ground states). For some elements, the atomic masses of different atoms are not the same because of differences in the number of neutrons. Atoms of an element with different numbers of neutrons are known as "isotopes". For example, one isotope of carbon (^{12}C) has 6 protons and 6 neutrons and an atomic mass of 12 exactly (by definition), whereas another isotope of C (^{13}C) has 6 protons and 7 neutrons and an atomic mass of 13.003354838. For any given sample that contains a mixture of ^{12}C and ^{13}C atoms, the "atomic weight" (or "relative atomic mass") of the element C in the sample is equal to the mean value of the atomic masses of all the atoms of ^{12}C and ^{13}C in the mixture. The atomic weight of element E in a sample p ($A_r(E)_p$) therefore depends not only on the atomic masses of the different isotopes, but also on the relative numbers of the isotopes in the sample:

$$A_r(E)_p = \sum[x(^iE) \cdot A_r(^iE)]$$

where $x(^iE)$ is the mole fraction of isotope ^iE and the summation is over all stable isotopes of the element.

Furthermore, because the relative abundances of ^{12}C and ^{13}C atoms in different samples containing carbon may be different, the element C does not have a uniquely defined atomic weight that applies to all samples containing C. For example, if the carbon atoms in a sample are 99 % ^{12}C and 1 % ^{13}C, the atomic weight of C in that sample is approximately 12.01. In

another sample with 98 % ^{12}C and 2 % ^{13}C, the atomic weight of C would be about 12.02. Variations of this sort can be a result of chemical and physical processes that cause "isotope fractionation" in both natural and synthetic materials. Therefore, although the atomic weight of an element like C in a specific sample may be known precisely if the isotope amount ratios are known, other samples that have not been analyzed for isotopic composition could have a range of carbon atomic weights. This type of "uncertainty" in the atomic weight of C is not a result of poor measurements, but rather is a result of real variations in the isotopic composition of different samples that must be recognized by IUPAC when recommending atomic weights of the elements and by users of the atomic weight tables. For other elements that do not exhibit measurable isotopic variation, the uncertainties of the atomic weights are more closely related to the measurement uncertainties of the atomic masses or the isotope-amount ratios.

The "Standard Atomic Weight" value and its associated "uncertainty" are evaluated quantities assigned by IUPAC (CIAAW) to encompass the range of possible atomic weights of an element that might be encountered in all samples of normal terrestrial materials. The uncertainty (or interval) of the Standard Atomic Weight of an element is based on either the measurement uncertainty of the atomic weight in a representative sample, or the interval over which known variations in atomic weights among normal terrestrial materials have been reported, whichever is larger. Normal terrestrial materials are understood to include both natural specimens and common chemical reagents; that is, all types of specimens that may be encountered in a laboratory engaged in chemical analysis.

Although the Periodic Table includes 118 elements, only 84 elements are given Standard Atomic Weights. To have a Standard Atomic Weight, according to long-standing Commission guidelines, an element must have at least one isotope with a half-life greater than 10^{10} yrs, which is comparable to the age of the universe.

Why do Standard Atomic Weights have varying uncertainties?

CIAAW's long-standing objective is to ensure the Standard Atomic Weights are as accurate and precise as possible, but with the provision that the tabulated values and their uncertainties (or intervals) include the vast majority of natural and artificial substances on Earth. As currently formulated, the Standard Atomic Weights have varying uncertainties and(or) intervals for the following reasons, as indicated in the accompanying Periodic Table of the Isotopes:

(1) For 36 elements, all known isotopes are radioactive with half-lives $< 10^{10}$ years. These elements are considered by CIAAW to have no "stable" isotopes and therefore do not have assigned Standard Atomic Weights. Exceptions to this rule are U and Pa, which have been given Standard Atomic Weights traditionally based on isotopes with shorter half-lives.

(2) For 21 elements that have only one stable isotope (half-life greater than 10^{10} yrs), the Standard Atomic Weights are equal to the atomic masses. The atomic masses are known relatively precisely from physical measurements (typically to within one part in 10^7 or better), although CIAAW traditionally added uncertainty coverage factors to the reported atomic mass uncertainties when assigning standard atomic weights to these elements.

(3) For 43 elements that have more than one stable isotope, the Standard Atomic Weights depend on the atomic masses and the relative abundances of the isotopes, and the uncertainties of the Standard Atomic Weights are mainly related to the evaluated uncertainties with which the isotope-amount ratios can be measured. Many of these elements are known to have varying atomic weights in different normal terrestrial materials because of precise relative measurements (i.e., differences in isotope amount ratios can be detected), but their Standard Atomic Weights are not affected by these variations because they are smaller than the evaluated uncertainties of the accuracy of the best isotope amount-ratio measurements (i.e., the actual isotope amount ratios in any one sample are more difficult to measure than differences between samples).

(4) For 18 elements that have more than one stable isotope, the known isotope-amount ratios differ from sample to sample in normal terrestrial materials by more than the evaluated uncertainties of the measurements. In these cases, the Standard Atomic Weights are reported as intervals (10 elements) or they are given expanded uncertainties (8 elements) to reflect these differences.

Because these different categories of elements exist, the Standard Atomic Weights recommended by CIAAW may change over time when new data become available. CIAAW may either decrease or increase the uncertainty as measurement accuracy improves or as wider ranges of variation are discovered.

The new Table of Standard Atomic Weights (with intervals)

Before 2009, the Commission on Isotopic Abundances and Atomic Weights and its predecessors listed single values for the Standard Atomic Weights with "uncertainty" values that reflected a combination of both measurement errors and natural isotopic variations. Although the accompanying documentation and footnotes provided clear distinctions between these different types of uncertainty, the Commission in 2009 decided to change the presentation of the Standard Atomic Weights to a format that highlights these differences more clearly. Specifically, elements for which known atomic weight variations exceed atomic weight measurement uncertainty are now given atomic weight intervals in the table, rather than single values with expanded uncertainties. In most cases, the tabulated intervals are not substantially different from the ones reported previously, but the new presentation emphasizes the fact that any given sample of an element could have an atomic weight different from that of another sample, and that the true atomic weight of a sample should be determined if it needs to be known precisely. It should be noted that the transition in the presentation of variable atomic weights was only partly completed in the 2009 TSAW. Intervals were reported for 10 elements for which the Commission had completed recent evaluations (mainly light elements with non-radiogenic stable isotopes), whereas expanded uncertainties were given for elements that are currently under evaluation (e.g., heavy elements and elements with radiogenic isotopes). It is anticipated that future versions of TSAW will provide intervals for more elements, as well as updated intervals and uncertainties for all of the elements, as these evaluations proceed.

ISOTOPIC VARIATIONS- CAUSES AND CONSEQUENCES

Introduction

There are approximately 3100 known isotopes of the 118 elements in the Periodic Table (Figure 1, Periodic Table of the Isotopes). 283 of the isotopes are stable or have half-lives greater than 10^{10} years (comparable to the age of the universe) (Figure 2, Chart of the Nuclides). All stable or quasi-stable isotopes are included in the evaluation of the Standard Atomic Weights for the 82 elements that have them. The vast majority of known isotopes (approximately 2800) are radioactive with half-lives less than 10^{10} years, and majority of these have half-lives less than 1 minute. Many of the radioactive isotopes do not occur naturally on Earth, but can be produced by artificial nuclear reactions. The enormous diversity of stable and radioactive isotopes provides a wealth of practical tools for science, industry, health, and safety. The interactive Periodic Table of the Isotopes gives examples of specific uses of isotopes for each of the elements separately. Here we summarize briefly some of the causes of isotopic variation of the elements. Isotopic variations begin with the stellar processes through which the elements are formed. Subsequent changes in isotopic abundances are caused by radioactive decay, other nuclear reactions, and various physical-chemical-biologic processes of isotopic fractionation. This discussion leads to an overview of how isotopes are used to solve scientific and practical problems in the following section.

Nucleosynthesis (origins of elements/isotopes in the stars)

Stars are busy doing what alchemists could only dream of and creating new isotopes by mixing together nuclei in exotic, high-energy nuclear reactions. The distribution of the isotopes of the elements can enlighten us how they were formed in the first place. So, for centuries, scientists have studied the chemical composition of the rocks of our Earth to search for clues. The problem is that the Earth is very old and very active. Geological processes such as volcanoes and the weathering of rocks and minerals by water and air have erased much of the evidence. A more promising source of information is found in meteorites, the fragments of debris and asteroids in our Solar System that fall to Earth in fiery displays. Meteorites are excellent archives of the material that collected to form our Solar System and the processes responsible for building the planets. We can also look at the light from the Sun. The different wavelengths (or colors) that make up sunlight contain hints about the elements actually in the Sun.

So, what have we learned from these extra-terrestrial clues? Stars are element factories, continuously burning lighter nuclei, such as hydrogen (^{1}H) to form heavier nuclei like helium (^{4}He) and releasing tremendous amounts of energy in the process. This energy not only powers the nuclear reactions in the sun, but also is responsible for the light and heat that we feel here on Earth. The *nuclear fusion* of hydrogen is called hydrogen burning where four protons (^{1}H nuclei) combine to form a ^{4}He nucleus. This is the major process occurring in the interior of our Sun. In more massive stars, where ^{12}C nuclei are present, the fusion of four protons to one ^{4}He nucleus also happens, using ^{12}C as a catalyst in the *CNO cycle*. A catalyst

is a substance that is neither consumed nor produced, but necessary for the reaction to occur. Minor amounts of ^{14}N can be produced by the CNO cycle.

At some point, the star will use up its supply of protons in the core and proton fusion then ignites in the shell around the star. The star enters the Red Giant stage of its existence. If the star is sufficiently massive, the fusion of ^{4}He, so-called *helium burning*, can begin in the core of the Red Giant and form nuclei including ^{16}O, ^{20}Ne, and ^{24}Mg. In old Red Giant stars, the fusion of ^{12}C nuclei will build nuclei such as ^{20}Ne, ^{23}Na, and ^{24}Mg. Other nuclear reactions will create nuclei of ^{28}Si, ^{32}S, ^{36}Ar, ^{40}Ca. For very massive stars, the fusion of oxygen and even silicon nuclei is possible, forming isotopes of vanadium, chromium, manganese, cobalt, nickel, and iron.

The production of energy through fusion reactions ceases once it is no longer possible to release energy by combining two nuclei to form a single nucleus. This will occur with isotopes of ^{56}Fe. The heavier elements are produced when lighter nuclei *capture neutrons slowly* over timescales on the order of hundreds of thousands to millions of years. If the neutron-rich nuclei that are formed are stable with respect to beta decay (transformation of a neutron to a proton, electron and anti-neutrino), the newly created isotopes continue to capture additional neutrons. If the new nucleus is not stable with respect to beta decay, the nucleus will undergo radioactive decay to form a new chemical element. Some nuclei have *magic numbers* of protons and neutrons and these isotopes are found in relatively high abundance. Magic numbers of nucleons are 2, 8, 20, 28, 50, 82 and 126 and correspond to filled nuclear shells, similar to the concept of filled electronic shells in atoms.

Very massive stars go out with a bang. These stars collapse and explode violently as a supernova and release incredibly large amounts of energy. The supernova explosion observed by Earthlings in 1987 (SN1987A) produced more energy in the first ten seconds than our Sun will produce over its 10 billion year existence! The supernova produces large numbers of neutrons, which are captured by nuclei very quickly, on the order of seconds or less. This *process occurs so rapidly*, that neutrons are added to the nucleus before beta decays can occur. Eventually, the probability of capturing another neutron becomes so small that the nucleus decays to a new element (a nucleus with one less neutron, but one additional proton). A succession of neutron capture and beta decay will occur until a stable nuclear configuration is formed. The rapid capture of neutrons will terminate at mass 254, at which point an additional neutron is more likely to split the nucleus into two or more smaller nuclei (*fission*) than produce a heavier isotope.

Other less common processes can also form nuclei. For example, cosmic ray particles and protons bombard heavier nuclei in the interstellar medium. These high-energy collisions can fragment the nucleus into smaller pieces. *Spallation* reactions are thought to be the mechanism that produces isotopes of lithium, beryllium, and boron.

Radioactivity

Some isotopes are either **radioactive** (subject to radioactive decay), or **radiogenic** (a product of radioactive decay), or both. Radioactive isotopes decrease in abundance according to the **radioactive decay** equation:

$$(N / N0) = e^{-\lambda t}$$

where N0 and N are the initial and measured (after time t) numbers of atoms of a radioactive isotope, respectively, and λ is the decay constant, in units of t^{-1}. The half-life of a radioactive isotope (time for half of the original atoms to decay) is given by:

$$T_{1/2} = \ln(2) / \lambda.$$

In the absence of other fractionating processes, radioactive decay alone can alter the isotopic composition and atomic weight of the parent element over time, but it may not necessarily lead to variations among different samples at a given time (such as the present) because all occurrences have decayed at the same rate. For example, the radioactive decay of ^{87}Rb ($T_{1/2}$ = 2.1 x 10^{-11} a^{-1}) is calculated to have caused the $n(^{87}Rb)/n(^{85}Rb)$ ratio to change by about 6 % in the 4.56 x 10^9 a since the formation of the Earth, but all occurrences of Rb of terrestrial origin sampled within historic times have essentially the same value of $n(^{87}Rb)/n(^{85}Rb)$, hence the same atomic weight.

Radioactive decay can cause large variations in the isotopic composition of the element that includes the product isotope. Stable radiogenic isotopes increase in abundance as the products of radioactive decay:

$$N^* = N0 [1 - e^{-\lambda t}]$$

where N^* is the number of atoms of the product (radiogenic) isotope after time t. The magnitude of the change in the isotopic composition of an element with a radiogenic isotope largely depends on the age of the sample and the relative abundances of the parent and product element in a sample, which can vary widely as a result of geochemical processes. For example, decay of ^{87}Rb to ^{87}Sr can cause a substantial increase in the $n(^{87}Sr)/n(^{86}Sr)$ ratio of a material with a large n(Rb)/n(Sr) ratio, but will have relatively little effect on the $n(^{87}Sr)/n(^{86}Sr)$ ratio of a material with a small n(Rb)/n(Sr) ratio. Furthermore, the magnitude of the change in the Sr isotope-abundance ratio of any substance caused by the decay of Rb will depend on the period of time the substance has had its present form, and the extent to which it has approximated a closed system. Because specific minerals typically crystallize with different n(Rb)/n(Sr) ratios, it is possible to have variations in the $n(^{87}Sr)/n(^{86}Sr)$ ratio within individual rock samples. The most extreme variations in the isotope-abundance ratios of Sr and other elements with radiogenic isotopes are likely to be found at relatively small scales of observation, such as in individual mineral grains. This is especially evident for some of the noble gases (e.g., He, Ar), which may be almost entirely radiogenic in some occurrences. Reported variations in the isotope abundances of many elements are increasing with development of microprobe techniques in mass spectrometry.

Some types of nuclear transformations other than radioactive decay also can cause variations in the abundances of certain isotopes. For example, interactions of energetic cosmic ray particles with the atmosphere and with the Earth's surface produce a large number of **cosmogenic** isotopes by nuclear reactions such as spallation (a nuclear reaction with more than one product nucleon) and neutron capture. Some well-known cosmogenic isotopes like ^{14}C and ^{36}Cl are radioactive (with half-lives of $T_{1/2}$ = 5730 a, and 301000 a, respectively) and are used in geochronology. Typically, the abundances of isotopes such as these are many orders of

magnitude smaller than the abundances of the major isotopes and they would have negligible effect on the atomic weights of the elements in materials in which they are normally found.

Artificially produced radioactive isotopes are among the most useful and important products of modern industry. Various products of radioactive decay have different properties that can make them useful and (or) dangerous, for example:

neutron (n) Interacts with surrounding atoms, commonly causing nuclear transformations, can cause induced radioactivity

electron (β-), positron (β+)- Interacts with surrounding atoms, commonly causing ionization, travel distance short but variable

alpha particle (2p+2n)- Relatively massive, interacts with surrounding atoms, commonly causing ionization, can cause induced radioactivity, travel distance short

gamma (γ)- Electromagnetic radiation, less direct interaction with surrounding atoms, secondary ionization by photoelectrons, longer travel distance

Isotope fractionation

Isotopes of some elements may be separated preferentially from each other ("**isotope fractionation**") by physical, chemical, or biological processes, the rates or equilibrium states of which are mass dependent. Processes that differentiate on mass, and that commonly yield measurable changes in isotopic composition, include changes of physical state (e.g. evaporation, condensation, crystallization, melting), ion exchange, sorption and desorption, diffusion, ultra-filtration, and a variety of biological processes including photosynthesis, assimilation, respiration and dissimilatory oxidation-reduction reactions. Isotopic effects of these processes commonly are relatively large and readily detected in the case of "light" elements. For example, as early as 1939, it was shown that the $n(^{13}C)/n(^{12}C)$ ratios in various samples of C varied by up to 5 % of that ratio. The atomic weight of C in any given sample is therefore dependent on the source of the C and the extent of C isotope fractionation in the sample prior to analysis. Heavier elements are subject to similar processes, but the isotope fractionation effects commonly are smaller because the relative mass differences between the different isotopes are smaller than in the light elements. In addition to the common mass-dependent isotope fractionation effects, there are some processes that result in non-mass-dependent isotopic variation. Such variations are especially noticeable in some atmospheric constituents such as ozone, but recent studies have opened new frontiers in the subtleties of isotope fractionation processes and their applications.

Equilibrium isotope fractionation results when the forward and backward reaction rates are the same between multiple coexisting phases or species with a common element. The equilibrium isotope fractionation factor (α) is given by:

$$\alpha_{a/b} = Ra / Rb$$

where a and b are two chemical species in isotopic equilibrium and R is the abundance ratio of two isotopes of an element ($R = n(^{i}E)/n(^{j}E)$, where ^{i}E and ^{j}E typically are the heavier and lighter isotopes of an element, respectively). The factor α is related to the thermodynamic equilibrium constant for the isotope exchange reaction between two isotopes of the element E.

Kinetic isotope fractionation results from differences in the dissociation energies of isotopically different molecules of a given chemical species undergoing an irreversible transformation. The kinetic isotope fractionation factor commonly is designated either in the same way as the equilibrium fractionation factor ($\alpha_{a/b}$, where a is the product species and b is the reactant species), or as its reciprocal ($\beta = 1/\alpha$). Kinetic fractionation can also be expressed as the ratio of the reaction rates of the two isotopically different molecules (or substrates) undergoing the reaction: $\alpha_{kin} = k^i / k^j$ where k^i and k^j refer to the reaction rates of molecules containing the heavier and lighter isotopes of the element in question.

The magnitudes of equilibrium isotope fractionations depend in part on state variables, temperature being the most important, whereas the magnitudes of kinetic fractionations commonly vary with the overall reaction rate and mechanism. Equilibrium isotope fractionation commonly results in heavier isotopes being concentrated in more oxidized compounds and in more condensed phases, whereas kinetic isotope fractionation generally results in lighter isotopes being concentrated in the products of the reaction and heavier isotopes concentrated in the residual (unreacted) molecules ($k^i < k^j$; $\alpha_{kin} < 1$). Measurements of mass-dependent fractionations of the stable isotopes of H, Li, B, C, N, O, S and Cl have been used in a wide variety of studies in the Earth sciences. As is the case with the radiogenic isotopes, some of the largest variations in isotope-abundance ratios caused by fractionation processes are commonly observed at relatively small scales, or in substances with low concentrations of an element.

Because natural variations in the isotopic compositions of the elements commonly are small and because the differences are easier to measure and commonly are more useful than the actual values, several different expressions have been used to amplify the differences and to obviate the need for "absolute" measurements for reporting purposes. Isotopic measurements of elements exhibiting isotope fractionation commonly are given with respect to a δ (delta) scale defined by:

$$\delta (^iE)_S = [R_S / R_{RM}] - 1$$

where R_S and R_{RM}, refer to the isotope-abundance ratios $n(^iE)/n(^jE)$ in a sample, S, and a reference material, RM, respectively. Delta values commonly are reported in parts per thousand, or per mill (‰), and measured by comparing the apparent isotope-abundance ratio in a sample with that of a reference material measured under precisely the same conditions, without an attempt to determine the "absolute" isotope-abundance ratios of either material. In this way, it is possible to detect useful isotopic variations with precision that is smaller than the measurement uncertainty of the techniques used to calibrate the atomic weights.

The relation between delta scales, isotopic abundances, and atomic weight values is illustrated by the large variations observed in H (Figure 3). Relative measurements of variations in $n(^2H)/n(^1H)$ are made by comparison to the isotopic reference material Vienna Standard Mean Ocean Water (VSMOW). A positive sign for $\delta(^2H)$ indicates that the sample is enriched in the isotope of higher mass compared to VSMOW. Isotope fractionation in H occurs largely because of vapor pressure differences between $^1H^1H^{16}O$ and $^1H^2H^{16}O$, and occurs when evaporation or condensation takes place, the magnitude depending on the temperature. As a result, the mole fraction of ^2H ($n(^2H)/[n(^1H) + n(^2H)]$) in H_2O on Earth ranges from about 0.000082 to 0.00025. Polar ice contains approximately two-thirds as much ^2H as ocean water.

The altitude of precipitation also affects the isotopic composition. Including all natural sources of H, the extreme values of the atomic weight are 1.007 851 to 1.008 010. Measured variations in $\delta(^2H)$ have provided useful information about natural processes in hydrology, meteorology, paleoclimatology, oceanography, and cosmochemistry.

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PRACTICAL USES OF ISOTOPES

Although it is difficult to classify the wide range of isotope applications into a few categories, some major types of uses are listed below, with some general information about the principles involved. Here we are concerned with applications that rely specifically on isotopic properties (e.g., radioactive decay, radiogenic isotope accumulation, isotope fractionation, specific isotope properties?), to the exclusion of the equally diverse set of applications based on the chemical properties of the elements, which are summarized in many other publications. Major categories of isotope applications include radioactivity and geochronology, stable isotope variation and Earth-system science, isotope forensics, isotope tracer experiments for environmental and health science, isotopes in industry, and isotopes in medical diagnosis and treatment.

Radioactivity and geochronology

Radioactivity provides a means for determining ages of things such as rocks, minerals, air and water masses, fossils, archeological objects, among many others. Knowing the relative amounts of radioactive (parent) and(or) radiogenic (product) isotopes corresponding to a decay scheme with known half-life, one can estimate the time elapsed since an object was formed and became a closed system. For example, a growing plant will incorporate small amounts of cosmogenic ^{14}C from the atmosphere in the CO_2 used for photosynthesis. When the tree dies, this process stops, and the ^{14}C in the plant remains will decay with half-life 5730 years. Thus, by analyzing the ^{14}C content (actually the ratio of ^{14}C to stable ^{12}C) in a piece of wood from an archeaological site, one could determine if the wood was more likely to be ancient or modern. This technique, also known as radiocarbon dating, has provided much of our information about ancient civilizations and human history, as well as rates of accumulation of sediments and peat deposits, movement of water through oceans and aquifers, and many other fields. It is important, when using such techniques, to know about possible complications related to exchange of C between the sample and its surroundings, changes in the concentration of cosmogenic ^{14}C in the atmosphere over time, and other processes that might affect the result. Air-borne testing of nuclear weapons during the late 1940s to early 1960s doubled the amount of ^{14}C in the atmosphere. This ^{14}C "bomb peak" can be quite useful for dating plants, soils, sediments, and water masses that are less than 60 years old. A variety of approaches may be taken to determine the ages of rocks and minerals. In one approach, the relative concentrations of radioactive K and radiogenic Ar can be compared to determine when a mineral crystallized from molten magma. Because the half life for radioactive decay of K is 1.248 e9 years, this technique works best for time scales ranging from millions to billions of years. The K-Ar technique works well if the rock contains a substantial amount of K, if the magma was degassed so it had little or no Ar when it crystallized, and if the radiogenic Ar was held tightly

in mineral grains while it accumulated by decay of K. Other forms of geochronology include measurements of cosmogenic isotopes to determine "exposure ages" of surface materials to cosmic rays, providing information about rates of erosion or history of glacial ice cover and climate change. In general, numerous assumptions must be addressed to make these sorts of determinations reliable. Nonetheless, many detailed studies involving various radioactive isotopes with different half-lives have established the principles of radioactive dating and geochronology since it was first proposed in the early 1900s. Some examples of questions that can be addressed by radioactive dating:

How old is the Earth?

When did the dinosaurs die off?

How long do ice ages last?

How often do volcanoes erupt?

Is our water supply sustainable?

Stable isotope variation and earth system processes

Variations in the stable isotopic composition of some elements have contributed greatly to our understanding in diverse scientific fields such as geology, volcanology, oceanography, sedimentology, atmospheric chemistry, hydrology, paleoclimate, biology, biogeochemistry, archaeology, among others. Elements most commonly used in such applications because of isotope fractionation include H, C, N, O, and S, which are relatively light and commonly are affected by oxidation and reduction reactions that discriminate on mass. For example, oxidized forms of C, N, O, and S (CO_2, NO_3^-, O_2, SO_4^{2-}) are all subject to reduction by bacteria in certain types of environments like saturated soils and wetlands. When these compounds are reduced (e.g., to CH_4, N_2, H_2O, H_2S), the reaction rates tend to be faster for molecules with lighter isotopes, such that the remaining unreacted oxidized compounds tend to become relatively enriched in the heavier isotopes. By measuring differences in the ratios of light to heavy isotopes of C, N, O, and S in these compounds, geologists, oceanographers, biologists, and hydrologists can determine where such reactions are taking place. Other types of isotopic variation are caused by radioactivity, through production of radiogenic isotopes that can act as natural tracers of element migration. As techniques have improved for sample preparation and isotope-ratio measurements, increasing numbers of elements have been used for such purposes, such that now almost all elements with multiple isotopes are being investigated for isotopic clues about Earth processes. The Periodic Table of Isotopes provides some clues about where to look next. Some examples of questions that can be addressed by stable isotope variations caused by isotope fractionation:

Is there life on Mars? (Where did life begin on Earth?)

How different were the temperatures during the ice ages?

Why do volcanoes behave differently (e.g., Why are some more explosive than others?)

What did early humans eat?

Is this ecosystem functioning properly?

Where should we look for strategic ore mineral deposits?

Forensic investigations using isotopes

Isotope forensics is based on the principles described above (isotope fractionation and radiogenic isotopes). Samples of any given substance can have different isotopic compositions because of isotopic compositions of materials used to make the samples were different, or because the processes used to make the samples fractionated the isotopes differently. Samples to be discriminated isotopically could be plants, animals, manufactured goods, foods, drugs, or just about anything. Isotopic "fingerprinting" may involve multiple isotope systems, and it can be combined with other techniques such as trace element or compound fingerprinting. An example of multiple isotope fingerprinting might be the analysis of animal hair or feathers for isotope ratios of H, C, O, N, S, and Sr, to detect geographically variable signatures of water, diet, or geologic setting (terroir) that might indicate where the animal had been recently. Such data can be used to study animal migration patterns, or to detect illicit transport of animal products. Similar analyses can be used to check the authenticity of the origin of products; for example, H and O isotope ratios in beverages may be related to the source of water (e.g., latitude or altitude of local precipitation), and C isotope ratios in sweets may be related to the source of sugar (e.g., beets, sugar cane). Isotopic analyses can sometimes be used to constrain responsibility and liability for industrial pollutants in the environment, as the isotopic signatures of pollutant sources may differ depending on industrial feed stocks or synthetic processes used by different producers. Applications of isotope forensics are diverse and growing rapidly. A few examples of questions that might be addressed with such data:
Is this wine really from France?
Is this orange juice fresh-squeezed or reconstituted?
Where has this criminal suspect been for the last 3 months?
Who is responsible for contaminating the water?
Is this country complying with nuclear test ban treaties?

Isotope tracer experiments for environmental and health science

Isotope tracers can be used to conduct experiments that track movement and reaction of specific elements and compounds. In tracer applications, isotopically enriched compounds are introduced into the system, where they may be transported, diluted, consumed, and transformed into other compounds. Processes affecting the isotopically labeled compound are assessed by analyzing various parts of the system to see where the enriched isotope went. Advantages of isotope tracers are related to the fact that they can be detected at low concentrations in isotope mixtures, thus providing good sensitivity without substantially disturbing the chemical makeup of the system. The isotopic "label" may be either a radioactive isotope that can be detected by its radioactivity, or a stable isotope that can be detected from anomalies in stable isotope ratio measurements. Radioactive tracers, such as ^{14}C, ^{3}H, or ^{35}S can be detected at extremely low abundances, providing sensitive tracers at very low concentrations. Radioactive tracers are more common in lab studies where they can be controlled and shielded from causing harmful effects in the surroundings. Small amounts of stable isotope tracers such as ^{2}H, ^{13}C, ^{15}N, ^{58}Fe, and ^{67}Zn are harmless and are more suitable for use in nutrition studies or in the environment where radioactive tracers may not be permitted. Isotope tracer experiments can be done in the laboratory, in humans, or in outdoor natural settings to answer a wide variety of questions, for example:
Is fertilizer being used efficiently?
Is natural remediation effectively removing contaminants from the water supply?
What is the most efficient form of iron supplement for human uptake?
How fast will anthropogenic atmospheric CO_2 be taken up into the ocean?

Isotopes in industry

Radioisotopes are used in industry in many ways, such as in radiography, in gauging applications, in mineral analysis, in flow tracing, in gamma sterilization for medical supplies, and for food preservation. Gamma radiography is used to scan luggage at airports. Gamma-rays show flaws in metal castings or welded joints. Critical components can be inspected for internal defects without damaging the component or making it radioactive. Unlike X-rays, radioactive sources are small and do not require power, so they can be transported easily to remote areas, where there is no power.

Radioisotope gauging uses the fact that radiation will be reduced in intensity by matter located between the radioisotope and a detector. The amount of the reduction can be used to gauge the presence or absence of the material or even to measure the quantity of material between the source and the detector. An advantage of this form of gauging is that there is no contact with the material being measured. For example, radioisotopes are used to analyze the contents of mineral samples, such as the continuous measurement of mineral slurry density in control of mineral processing the use of liquids to separate a metal from its ore. Gamma-ray transmission or scattering can determine the water content of coal on conveyer belts because the gamma-ray interactions vary with the atomic number (number of electrons) of the atom, hydrogen and oxygen versus carbon. Material coatings can be measured because some radiation is scattered back toward the radiation source and analysis of the back-scattered radiation provides information on the material's coating.

Radioactive tracers can be used to trace small leaks in complex systems such as power station heat exchangers. Flow rates of liquids and gases in pipelines, as well as large rivers, can be measured accurately with the assistance of radioisotopes.

It is estimated that smoke detectors are the most numerous of all devices that employ radioactive isotopes worldwide. Smoke detectors use ^{241}Am to ionize atoms of air (knock out external electrons from the atom), producing a small electrical current that is monitored. When smoke or steam enters the ionization chamber, it disrupts the current. The smoke detector senses the drop in current between the plates and sets off the alarm.

Isotopes in medical diagnosis and treatment

Nuclear medicine uses radioisotopes to provide diagnostic information about the functioning of specific human organs or to treat them. Radiotherapy can be used to treat some medical conditions, especially cancer, using radioisotopes to weaken or destroy particular targeted cells. The isotope ^{99}Mo, with half-life of 66 h, is used in approximately 80 % of all nuclear medical procedures. Every year in the USA, roughly 16 million patients undergo medical procedures that employ the ^{99}Mo decay product, metastable ^{99m}Tc {Kramer, 2011 #2937}.

Computed tomography (CT) or computed axial tomography (CAT) scanning is a medical imaging procedure that uses electromagnetic radiation (e.g., X-rays) to generate cross-sectional images of the body.

Positron emission tomography (PET) scans detect pairs of gamma-rays emitted indirectly by a positron emitting radioisotope (tracer). Images of these tracer concentrations in 4-dimensional space (time is the fourth dimension) within the body are reconstructed by computer analysis, often with the aid of a CT X-ray scan performed on the patient during the same session in the same machine.

Rapidly dividing cells are particularly sensitive to damage by radiation. Some cancerous growths can be controlled or eliminated by irradiating the area, a procedure called radiotherapy. In external radiotherapy, radiation is focused onto a target from outside the body. Internal radiotherapy is accomplished by administering radioactive substances or implanting a small radiation source in the target area. Short-range internal radiotherapy (brachytherapy) is becoming increasingly important as a means of targeted treatment. Many therapeutic procedures are palliative (intended to reduce symptoms but not to cure), for example to relieve pain, such as cancer induced bone pain. Radiotherapy may be preferable to traditional pain killers such as morphine because it improves patients' quality of life, allowing them to be more lucid during time spent with family.

Biochemical Analysis

It is easy to detect the presence or absence of radioactive materials even in very low concentrations. Radioisotopes are used to label molecules of biological samples in vitro (out of the body) to determine constituents of blood, serum, urine, hormones, antigens and many drugs. These procedures are known as radio-immuno-assays, such as using immunoglobulin molecules (monoclonal antibodies). These procedures help diagnose diseases such as diabetes, thyroid disorders, hypertension, and reproductive problems.

Diagnostic Radiopharmaceuticals

Radioactive products which are used in medicine are referred to as radiopharmaceuticals. Every organ in our body acts differently from a chemical point of view. A number of chemicals preferentially absorbed by specific organs are called targeting agents, such as iodine in the thyroid, strontium in bone, and glucose in the brain. When a radioactive form of one of these substances enters the body, it is incorporated into the normal biological processes and excreted in the usual ways, and its progress can be tracked. Radiopharmaceuticals can be used to examine blood flow to the brain, to evaluate functioning of the liver, heart, or kidneys, to assess bone growth, and to predict the effects of surgery and assess changes since a treatment has begun. In sports medicine, radiopharmaceuticals can be used to diagnose stress fractures, which are not generally visible in X-rays. The non-invasive nature of this technology with its ability to reveal organ function from outside the body makes this technique a powerful diagnostic tool.

Myocardial perfusion imaging uses radiopharmaceuticals for detection and prognosis of coronary artery disease. A distinct advantage of nuclear imaging over X-ray techniques is that both bone and soft tissue can be imaged successfully. By using nuclear imaging, physicians

can detect the presence of secondary cancer spread up to two years prior to detection by standard X-ray techniques.

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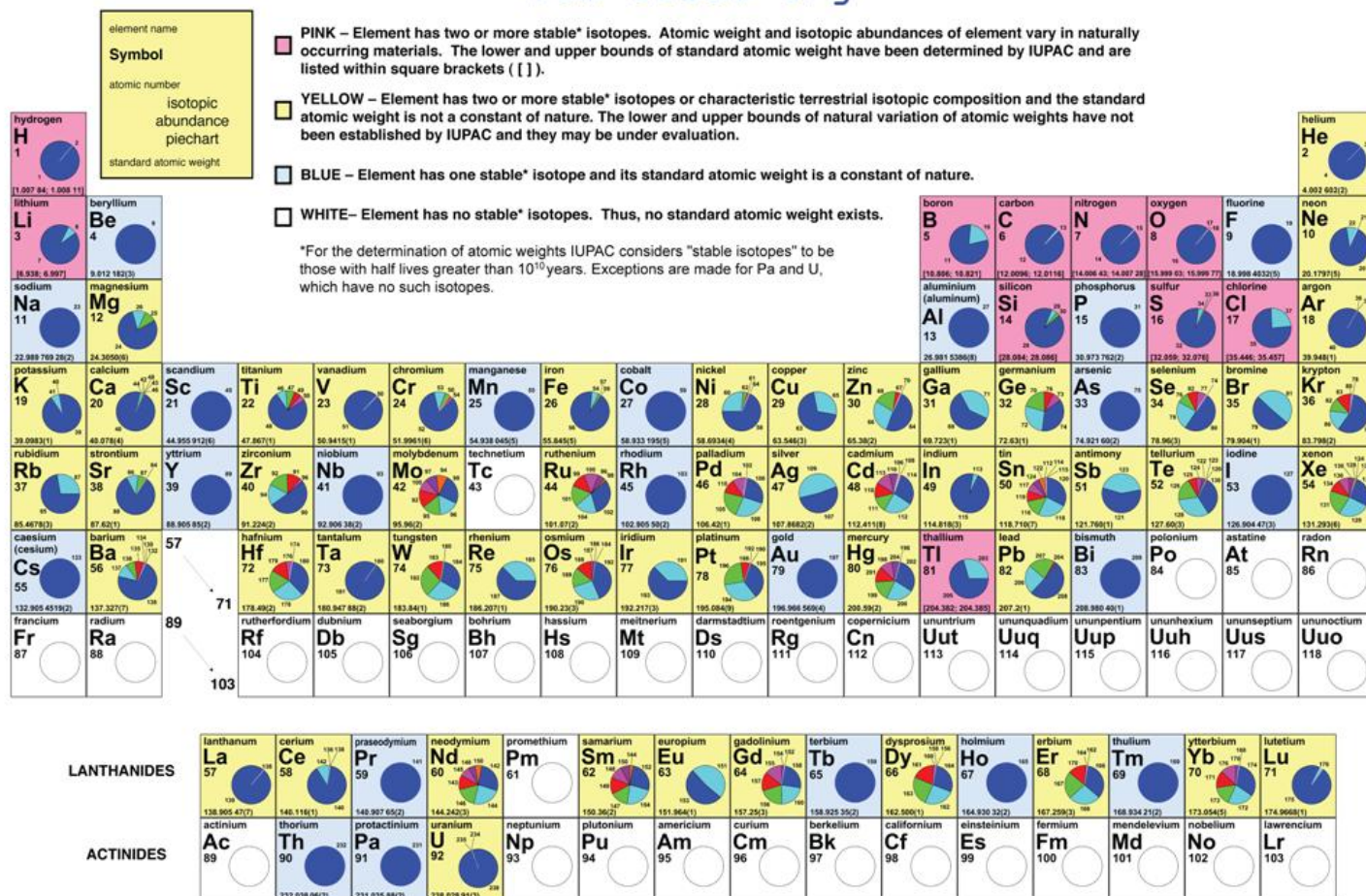
For more information: see WEBSITES

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Figure 1.

IUPAC Periodic Table of the Isotopes
www.ciaaw.org

Figure 2. Chart of the nuclides, showing the distribution of all stable and radioactive isotopes with respect to atomic number (Z, number of protons, on vertical axis) and isotope number (N, number of protons and neutrons, on horizontal axis). Isotopes in the dark center of the trend are stable, whereas those on the lighter fringes are radioactive.
http://www.nndc.bnl.gov/chart/
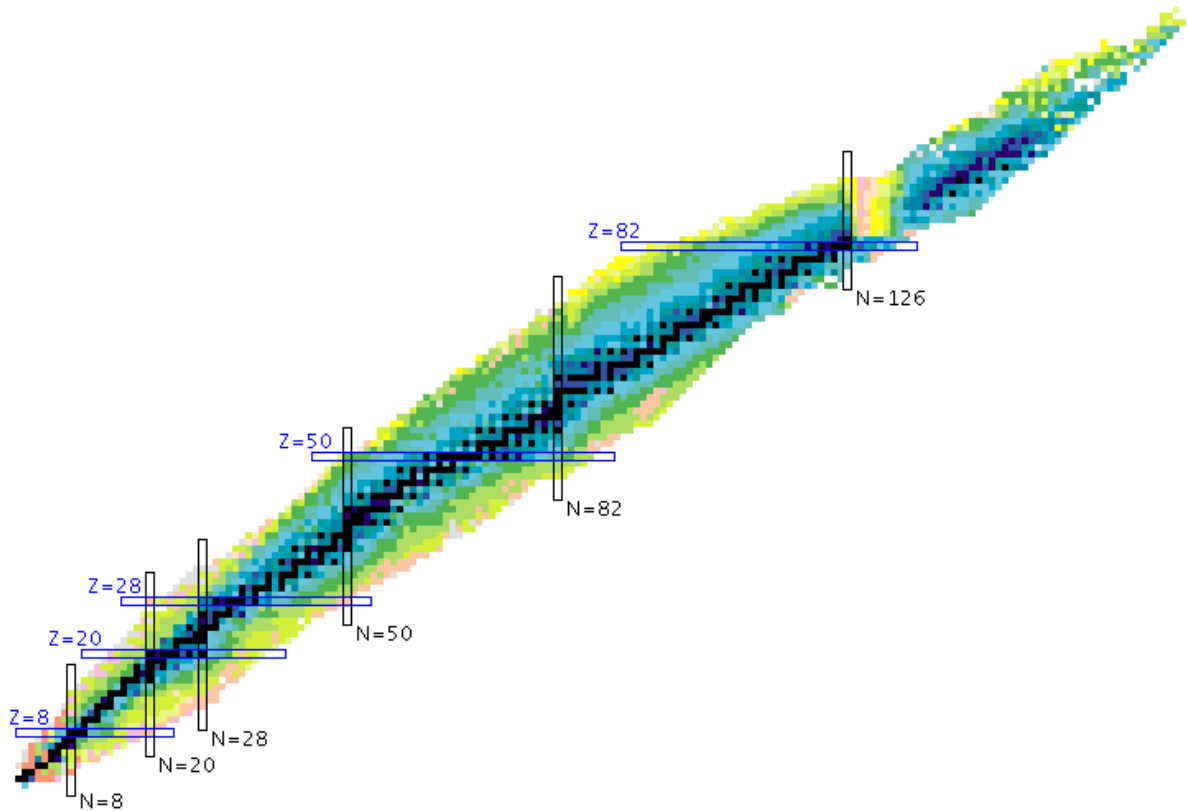
Figure 3. Variations in the isotopic composition and atomic weight of hydrogen in normal terrestrial materials.